22.4

Measures of Amine Basicity

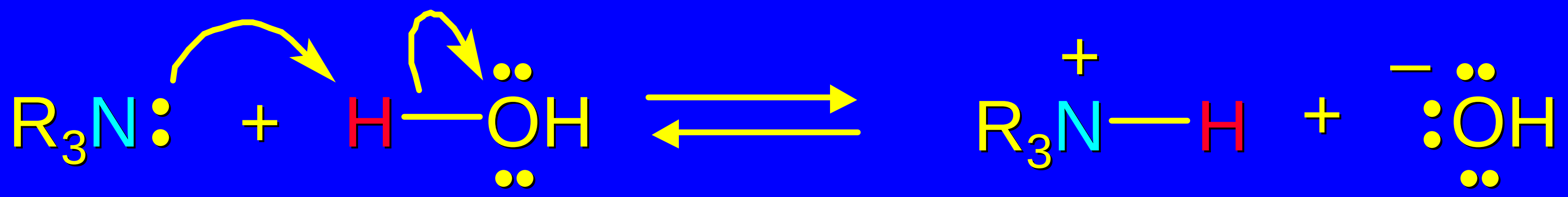
Measures of Basicity

The basicity of amines may be measured by:

1) K_b
2) pK_b
3) K_a of conjugate acid
4) pK_a of conjugate acid

Basicity Constant (K_b) and pK_b

K_b is the equilibrium constant for the reaction:



$$R_3N: + H{-}\ddot{\underset{..}{O}}H \rightleftharpoons R_3\overset{+}{N}{-}H + {}^{-}:\ddot{\underset{..}{O}}H$$

$$K_b = \frac{[R_3NH^+][HO^-]}{[R_3N]}$$

and $pK_b = -\log K_b$

K_a and pK_a of Conjugate Acid

K_a is the equilibrium constant for the dissociation of the conjugate acid of the amine:

$$R_3\overset{+}{N}\text{—}H \rightleftharpoons R_3N\colon + H^+$$

$$K_a = \frac{[R_3N][H^+]}{[R_3NH^+]}$$

and $pK_a = -\log K_a$

Relationships between acidity and basicity constants

$$K_a K_b = 10^{-14}$$

$$pK_a + pK_b = 14$$

22.5

Basicity of Amines

Effect of Structure on Basicity

1. Alkylamines are slightly stronger bases than ammonia.

Table 22.1 (page 866)
Basicity of Amines in Aqueous Solution

Amine	Conj. Acid	pK_a
NH_3	NH_4^+	9.3
$CH_3CH_2NH_2$	$CH_3CH_2NH_3^+$	10.8

Table 22.1 (page 866)
Basicity of Amines in Aqueous Solution

Amine	Conj. Acid	pK_a
NH_3	NH_4^+	9.3
$CH_3CH_2NH_2$	$CH_3CH_2NH_3^+$	10.8

$CH_3CH_2NH_3^+$ is a weaker acid than NH_4^+; therefore, $CH_3CH_2NH_2$ is a stronger base than NH_3.

Effect of Structure on Basicity

1. Alkylamines are slightly stronger bases than ammonia.
2. Alkylamines differ very little in basicity.

Table 22.1 (page 866)
Basicity of Amines in Aqueous Solution

Amine	Conj. Acid	pK_a
NH_3	NH_4^+	9.3
$CH_3CH_2NH_2$	$CH_3CH_2NH_3^+$	10.8
$(CH_3CH_2)_2NH$	$(CH_3CH_2)_2NH_2^+$	11.1
$(CH_3CH_2)_3N$	$(CH_3CH_2)_3NH^+$	10.8

Notice that the difference separating a primary, secondary, and tertiary amine is only 0.3 pK units.

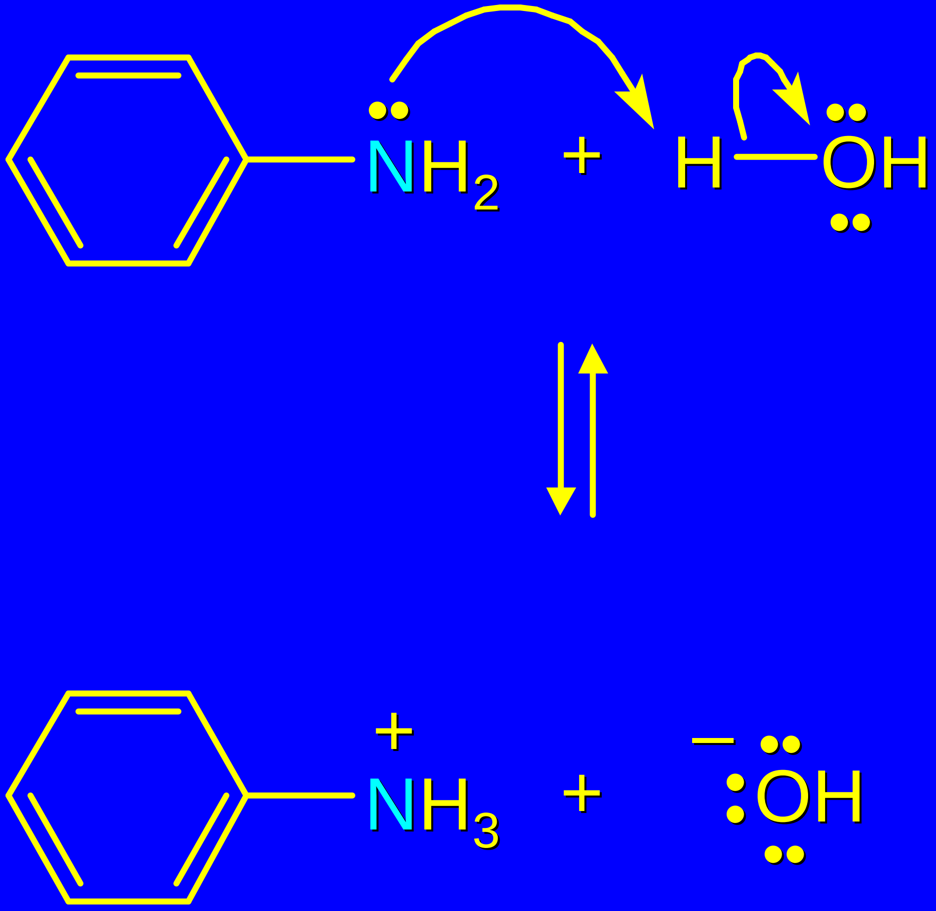
Effect of Structure on Basicity

1. Alkylamines are slightly stronger bases than ammonia.
2. Alkylamines differ very little in basicity.
3. Arylamines are much weaker bases than ammonia.

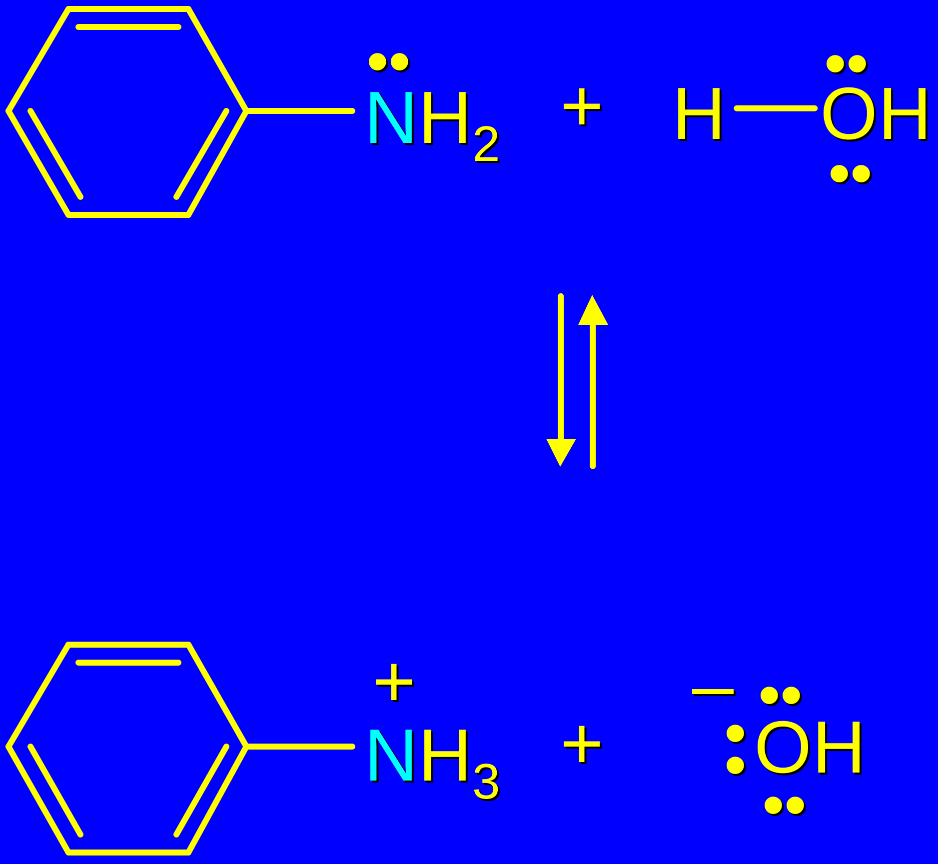
Table 22.1 (page 866)
Basicity of Amines in Aqueous Solution

Amine	Conj. Acid	pK_a
NH_3	NH_4^+	9.3
$CH_3CH_2NH_2$	$CH_3CH_2NH_3^+$	10.8
$(CH_3CH_2)_2NH$	$(CH_3CH_2)_2NH_2^+$	11.1
$(CH_3CH_2)_3N$	$(CH_3CH_2)_3NH^+$	10.8
$C_6H_5NH_2$	$C_6H_5NH_3^+$	4.6

Decreased basicity of arylamines



Decreased basicity of arylamines



Aniline (reactant) is stabilized by conjugation of nitrogen lone pair with ring π system.

This stabilization is lost on protonation.

Decreased basicity of arylamines

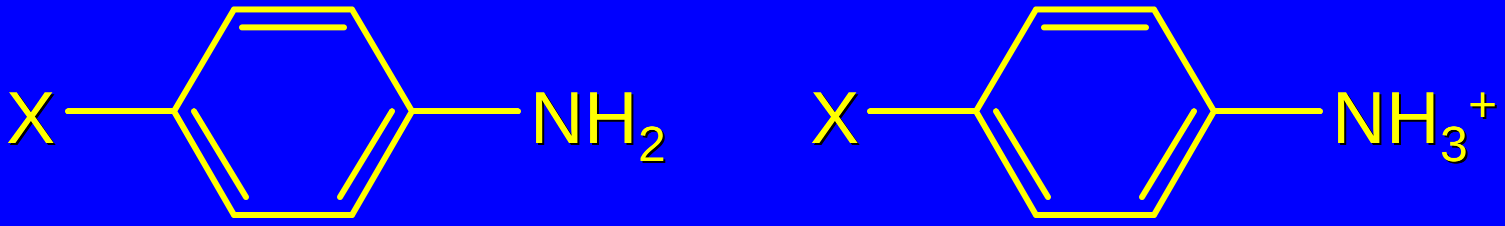
Increasing delocalization makes diphenylamine a weaker base than aniline, and triphenylamine a weaker base than diphenylamine.

	$C_6H_5NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
K_b	3.8×10^{-10}	6×10^{-14}	$\sim 10^{-19}$

Effect of Substituents on Basicity of Arylamines

1. Alkyl groups on the ring increase basicity, but only slightly (less than 1 p*K* unit).

Basicity of Arylamines

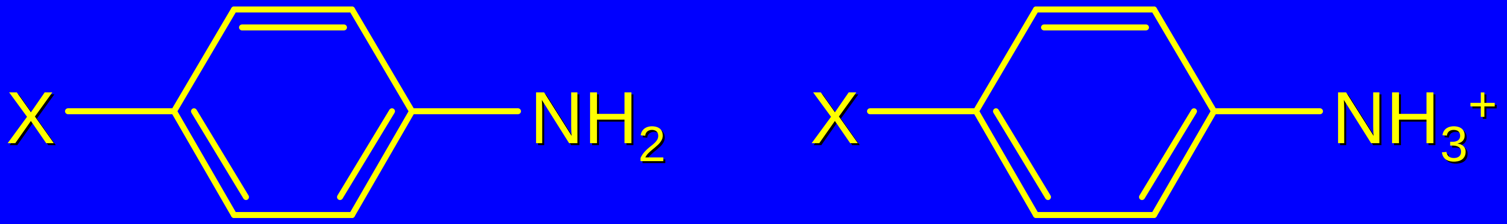


X	pK_b	pK_a
H	9.4	4.6
CH_3	8.7	5.3

Effect of Substituents on Basicity of Arylamines

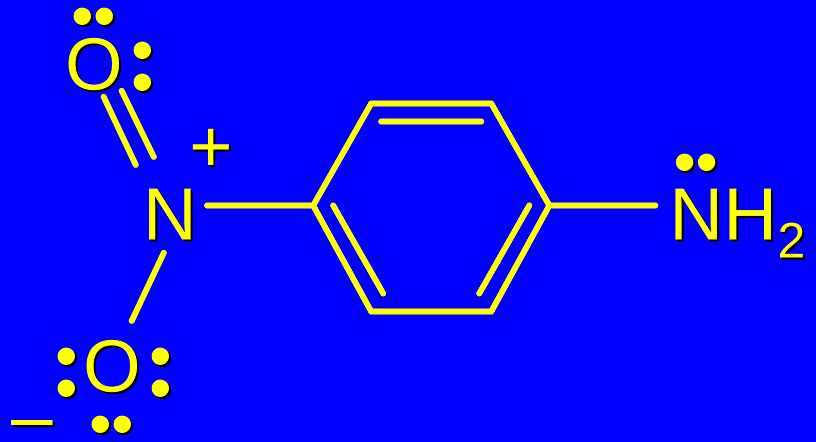
1. Alkyl groups on the ring increase basicity, but only slightly (less than 1 p*K* unit).
2. Electron withdrawing groups, especially ortho and/or para to amine group, decrease basicity and can have a large effect.

Basicity of Arylamines

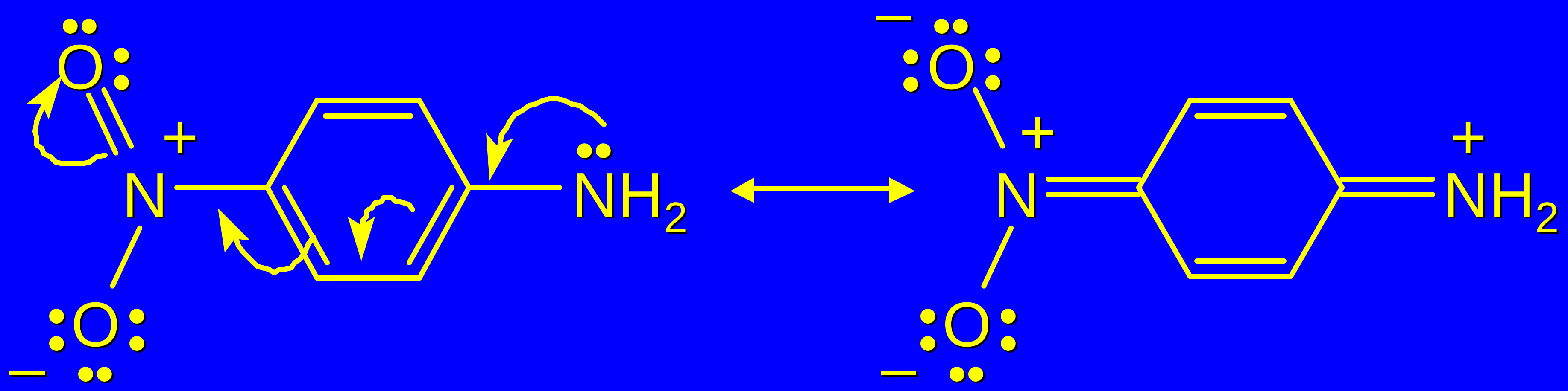


X	pK_b	pK_a
H	9.4	4.6
CH_3	8.7	5.3
CF_3	11.5	2.5
O_2N	13.0	1.0

p-Nitroaniline



p-Nitroaniline



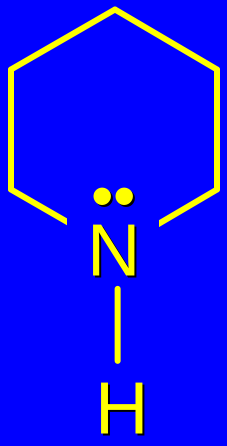
Lone pair on amine nitrogen is conjugated with *p*-nitro group—more delocalized than in aniline itself. Delocalization lost on protonation.

Effect is Cumulative

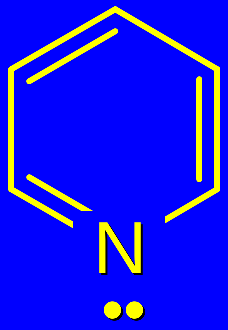
Aniline is 3800 times more basic than *p*-nitroaniline.

Aniline is ~1,000,000,000 times more basic than 2,4-dinitroaniline.

Heterocyclic Amines



is more basic than



piperidine

$K_b = 1.6 \times 10^{-3}$

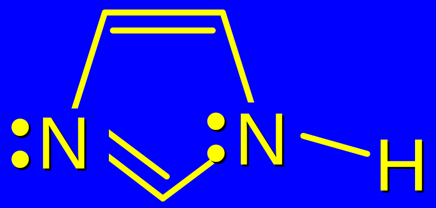
(an alkylamine)

pyridine

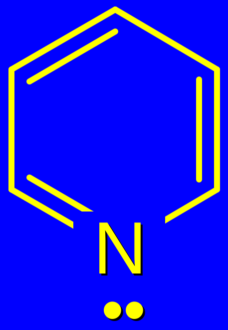
$K_b = 1.4 \times 10^{-9}$

(resembles an arylamine in basicity)

Heterocyclic Amines



is more basic than



imidazole

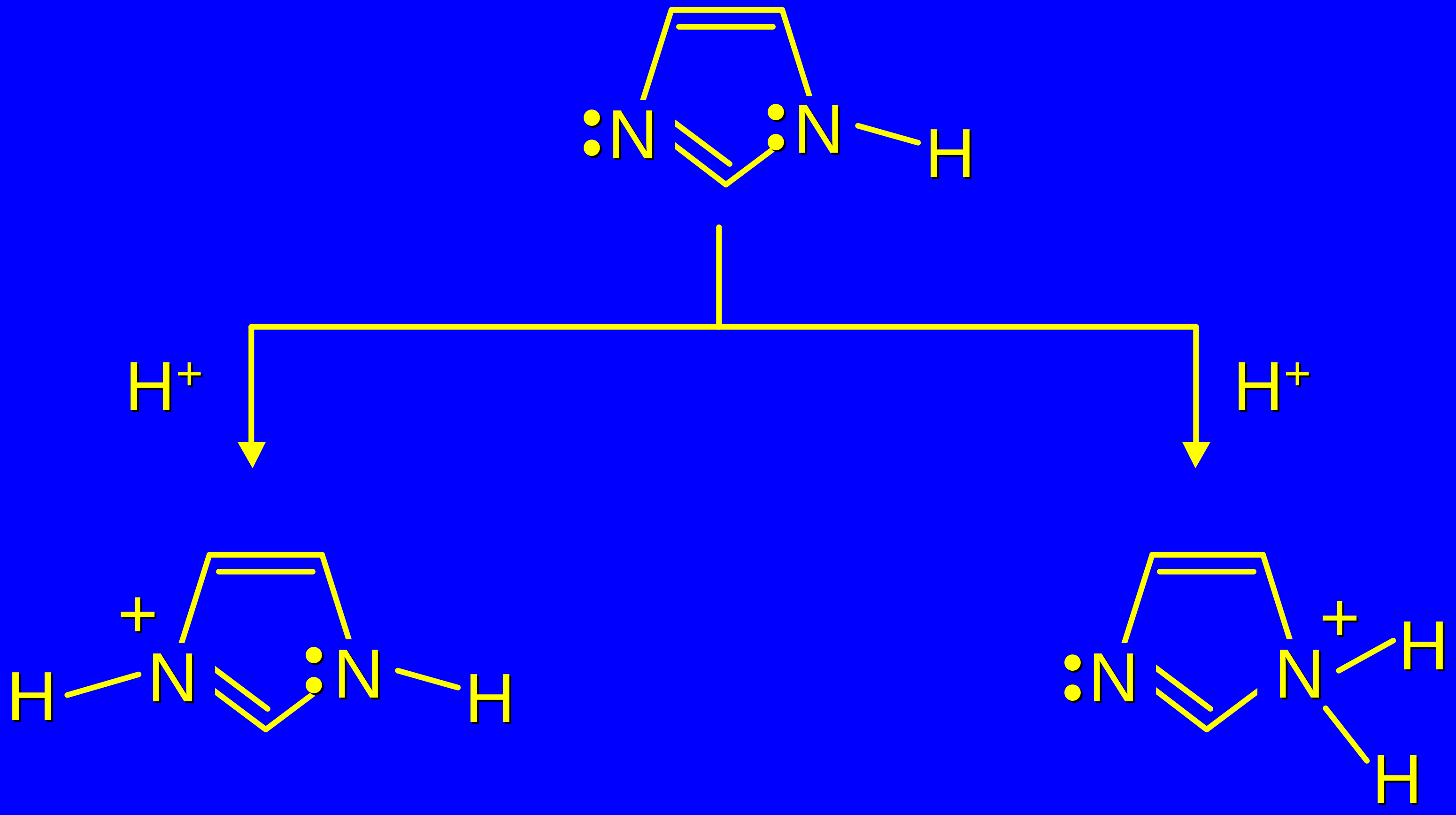
$K_b = 1 \times 10^{-7}$

pyridine

$K_b = 1.4 \times 10^{-9}$

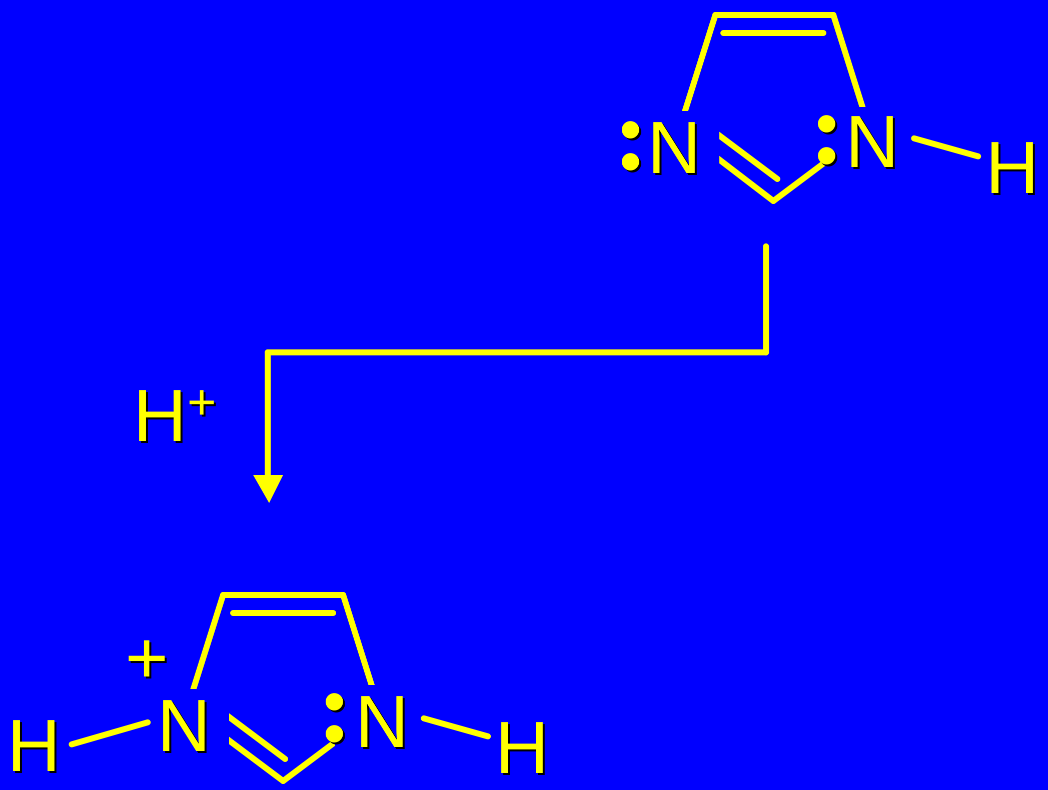
Imidazole

Which nitrogen is protonated in imidazole?



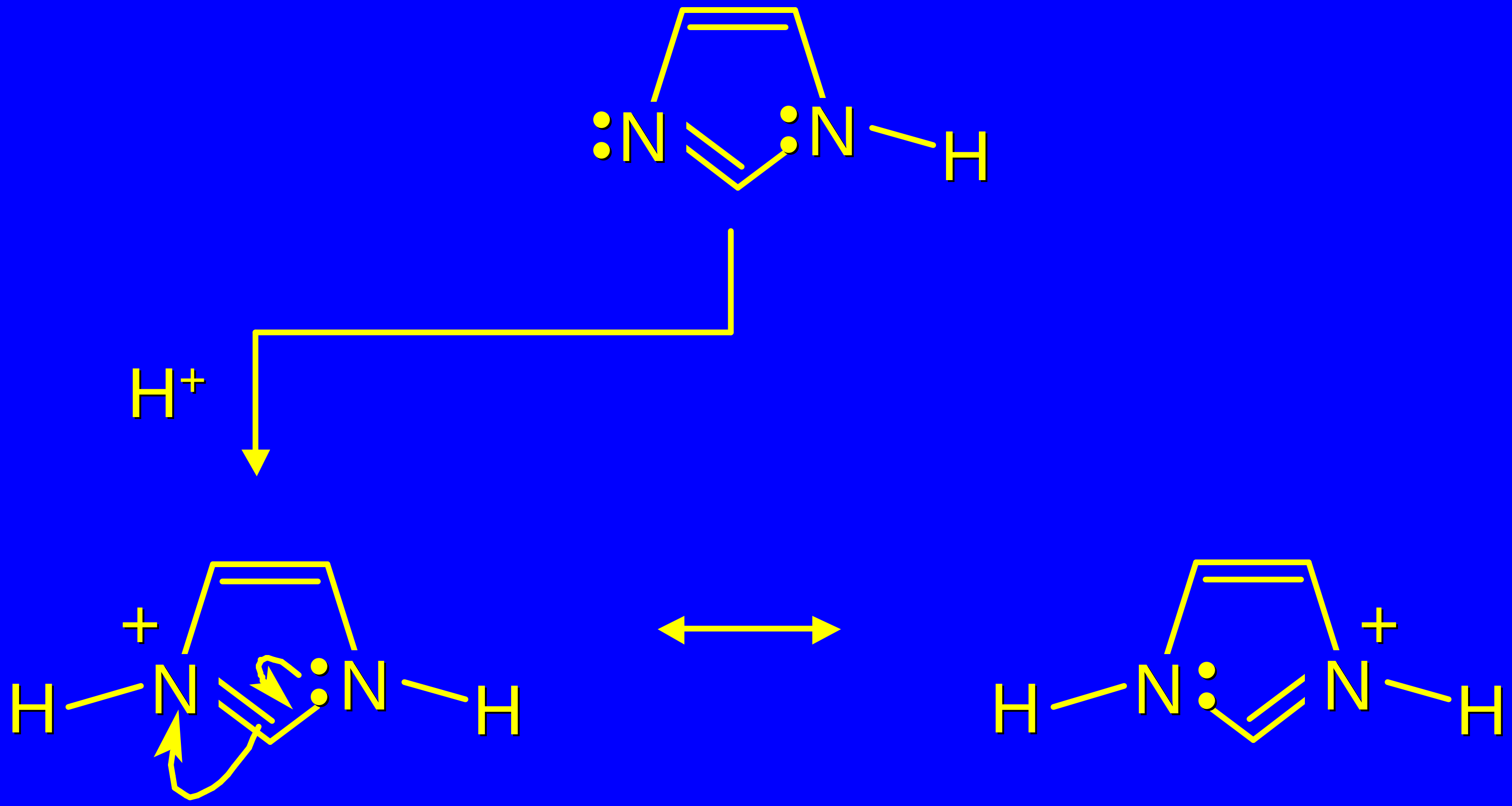
Imidazole

Which nitrogen is protonated in imidazole?



Imidazole

Protonation in the direction shown gives a stabilized ion.



22.6

Tetraalkylammonium Salts as Phase-Transfer Catalysts

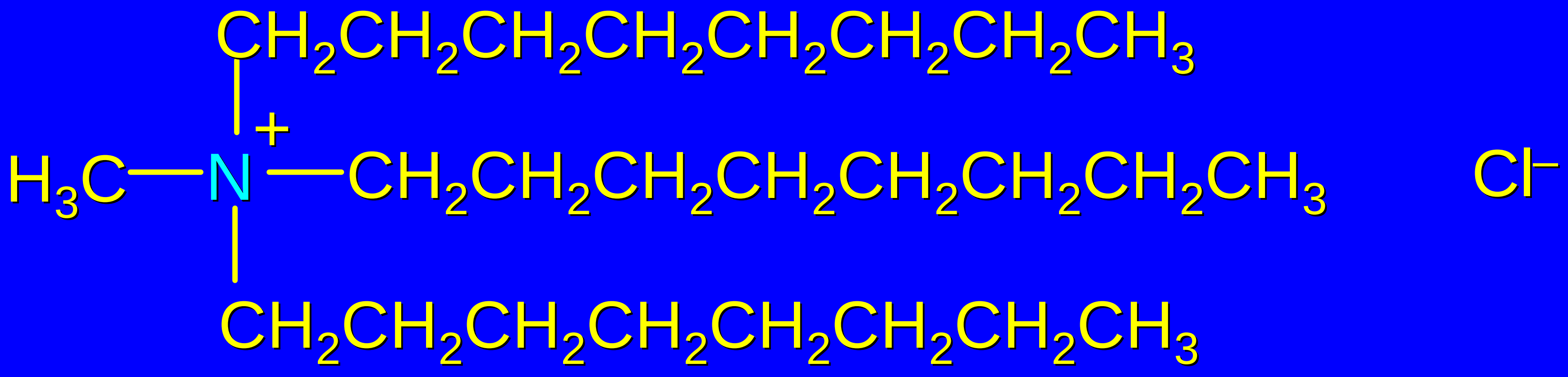
Phase-Transfer Catalysis

Phase-transfer agents promote the solubility of ionic substances in nonpolar solvents. They transfer the ionic substance from an aqueous phase to a non-aqueous one.

Phase-transfer agents increase the rates of reactions involving anions. The anion is relatively unsolvated and very reactive in nonpolar media compared to water or alcohols.

Phase-Transfer Catalysis

Quaternary ammonium salts are phase-transfer catalysts. They are soluble in nonpolar solvents.

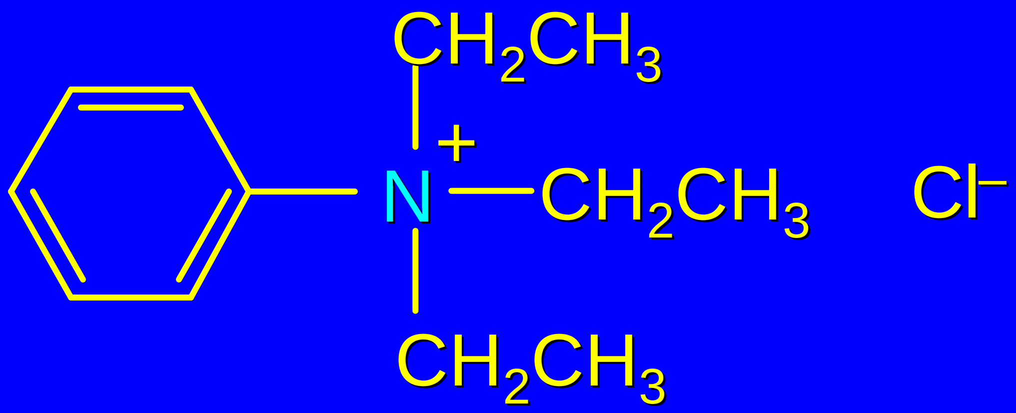


$$\mathrm{H_3C-\overset{\displaystyle CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3}{\underset{\displaystyle CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3}{\overset{+}{N}}}-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3\qquad Cl^{-}}$$

Methyltrioctylammonium chloride

Phase-Transfer Catalysis

Quaternary ammonium salts are phase-transfer catalysts. They are soluble in nonpolar solvents.



Benzyltriethylammonium chloride

Example

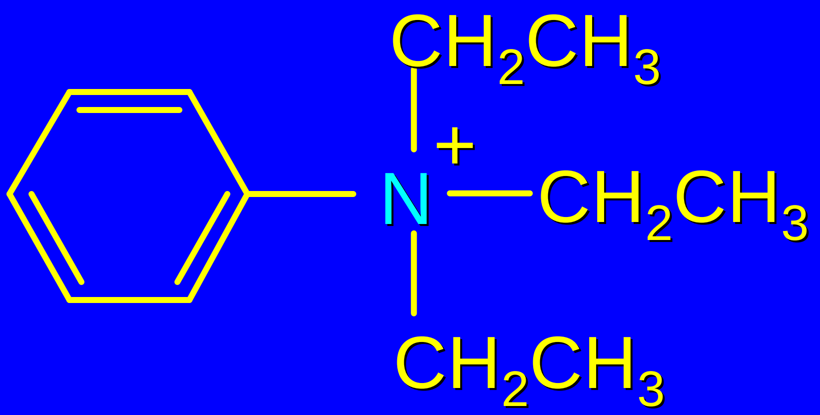
The S_N2 reaction of sodium cyanide with butyl bromide occurs much faster when benzyltriethylammonium chloride is present than when it is not.

$$CH_3CH_2CH_2CH_2Br \quad + \quad NaCN$$

$$\Big\downarrow \text{ benzyltriethylammonium chloride}$$

$$CH_3CH_2CH_2CH_2CN \quad + \quad NaBr$$

Mechanism

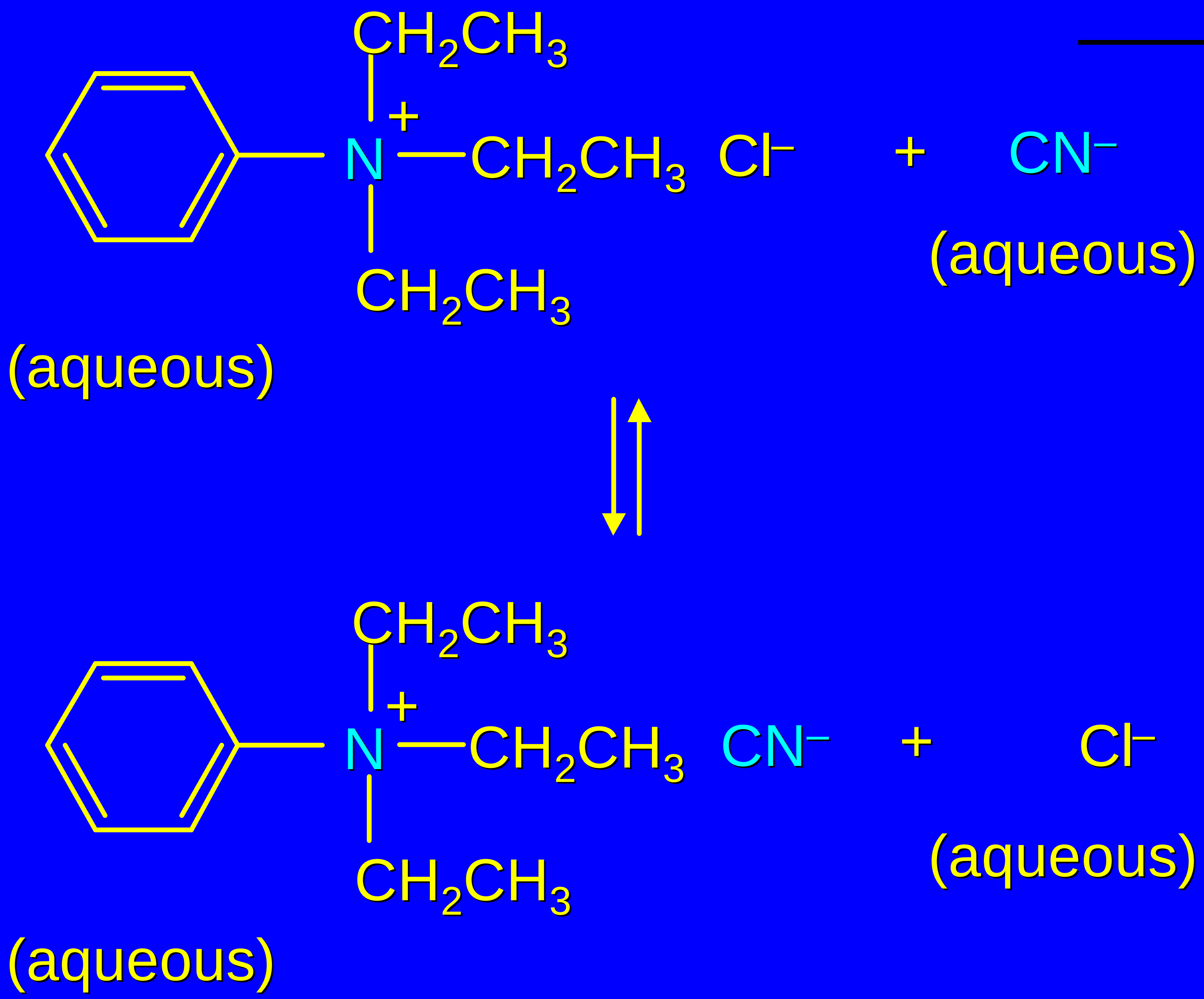


Cl^- + CN^-

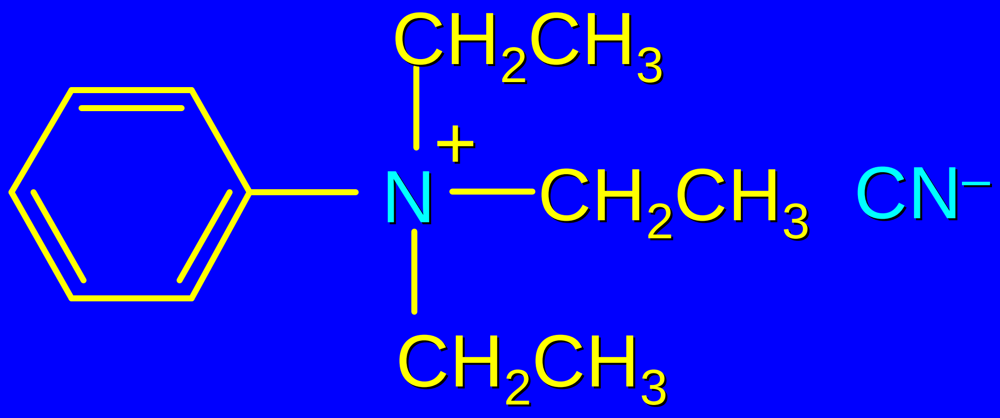
(aqueous)

(aqueous)

Mechanism

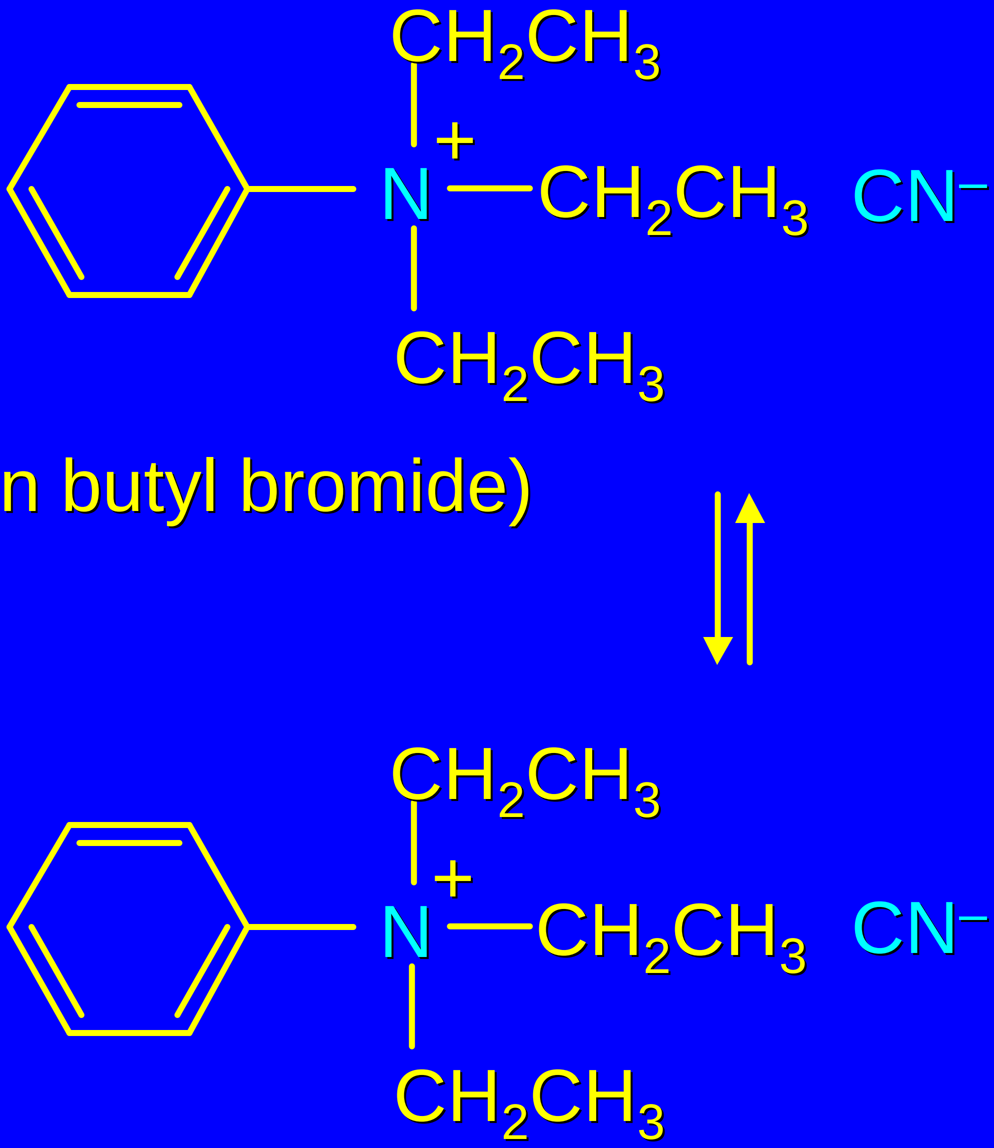

CH2CH3
+
N
CH2CH3
Cl–
CH2CH3
(aqueous)
+
CN–
(aqueous)
CH2CH3
+
N
CH2CH3
CN–
CH2CH3
(aqueous)
+
Cl–
(aqueous)

Mechanism



(aqueous)

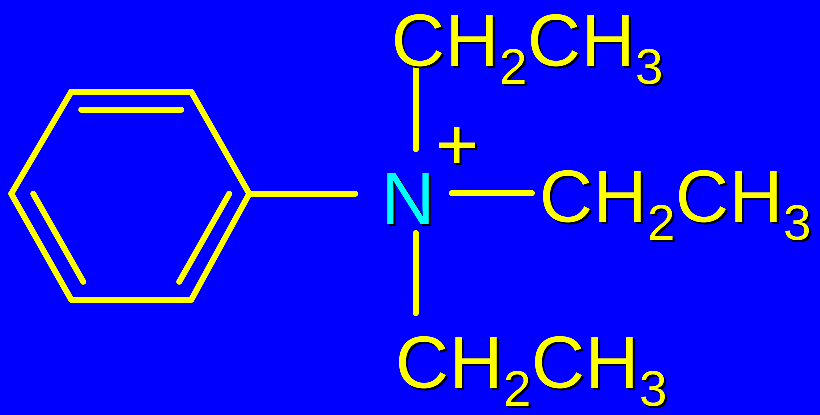
Mechanism



(in butyl bromide)

(aqueous)

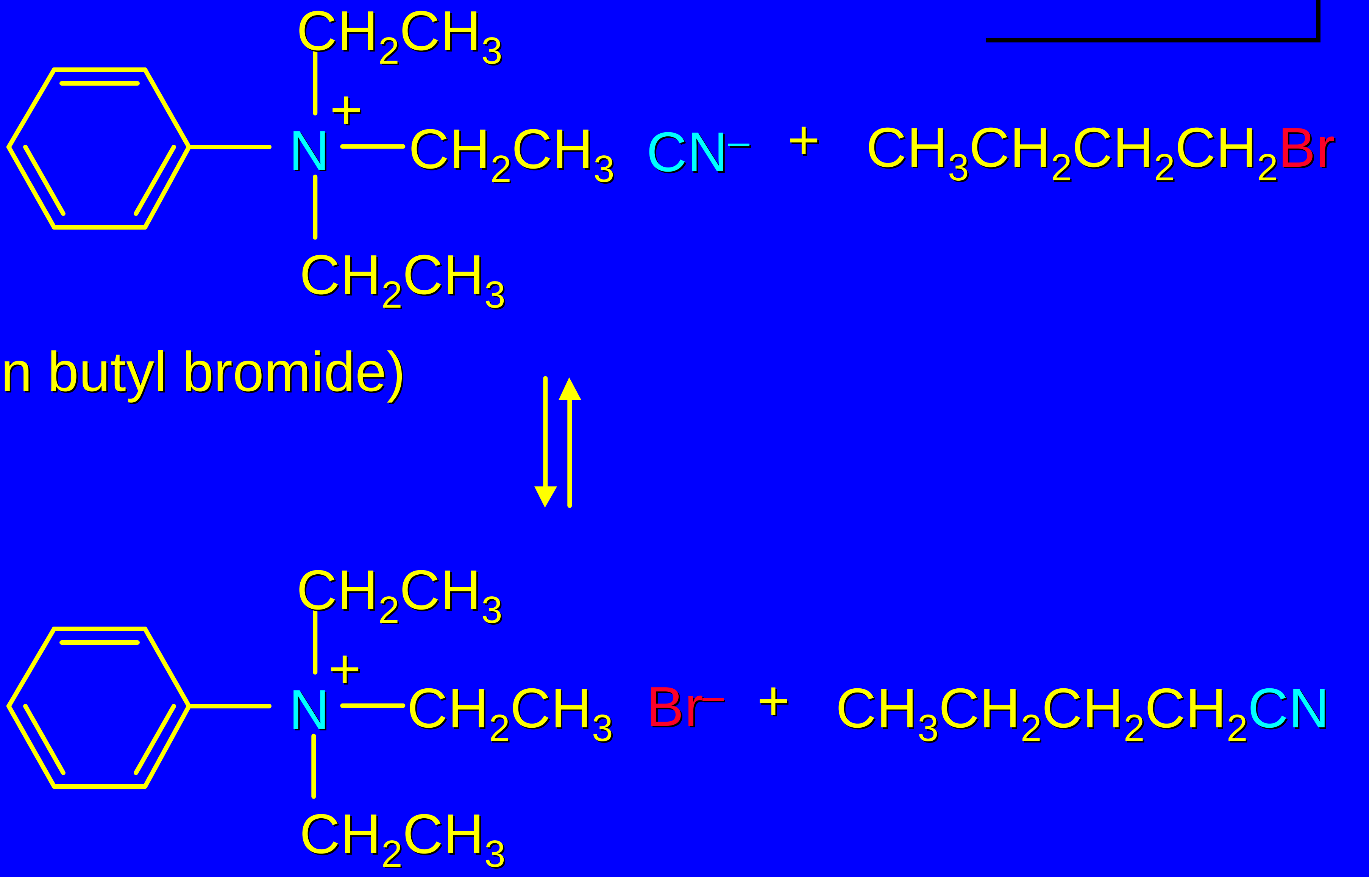
Mechanism



CN^{-} + $CH_3CH_2CH_2CH_2Br$

(in butyl bromide)

Mechanism



(in butyl bromide)

(in butyl bromide)